

6. RECYCLING

A. Recycling of Polymer Matrix Composites

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Objective

- Develop efficient and cost-effective processes for recovering carbon fibers from polymer matrix composites (PMCs).

Approach

- Continue the development and testing of processes to separate and recover carbon fibers from PMC scrap made with different thermoset and thermoplastic polymer substrates.
- Conduct an economic analysis of the process to determine its economic competitiveness.
- Work with a carbon fiber manufacturer to produce and test PMC panels made with recovered fibers and compare their properties with those of similar virgin-fiber panels.
- Recover carbon fibers for reuse in an automotive application.

Accomplishments

- Completed the development, evaluation, and testing of the thermal process to separate and recover carbon fibers from PMC scrap. The thermal method, a single-step process, recovered carbon fibers from PMCs made with different polymeric substrates with minimal changes in the properties of the original fibers. For most PMCs and mixtures of PMCs, the process is energy self-sufficient using the polymer substrate as an energy source.
- Conducted an economic analysis of the process, and it predicted a potential payback of less than 2 years, assuming a value of only \$1.5/lb of recovered carbon fibers.

- Recovered carbon fibers from “control” panels that were made by Hexcel Corporation,¹ with well-characterized carbon fibers, and the recovered fibers were sent back to Hexcel to re-make similar panels and to determine the suitability of the recovered fibers for making quality products. Hexcel found the fibers suitable for short fibers applications and reported that “Suggested applications of recycled carbon fiber are SMC (sheet molding compound), PEM (Proton Exchange Membrane for Fuel Cells), Batteries, and Concrete Reinforcement.”¹
- Oak Ridge National Laboratory (ORNL) also analyzed the fibers and found “the recovered carbon fibers from the ANL-pyrolytic based process—exhibit higher O/C chemical ratios than the corresponding virgin, treated but unsized—(finished product) carbon fibers. At the first moment, this result could indicate that these recovered fibers very likely will not require additional surface retreatment.”² Avoiding the need for retreatment of the fibers saves about \$0.40/lb of fibers.
- Produced more than 20 lb of recovered carbon fibers from two types of PMC scrap and shipped them to ORNL to be used in making an actual automotive application [skid plates for a sport utility vehicle (SUV)] using the Budd process.
- Published two articles^{3,4} describing the process. One of these publications⁴ received the Arch T. Colwell Merit Award. The award will be presented at the Honors Convocation during the SAE 2004 World Congress. A third publication⁵ is under preparation.
- Completed the project and accomplished its objective. The process developed and the characteristics of the carbon fibers that were recovered confirmed the technical feasibility and cost-effectiveness of recycling carbon fibers from PMCs into value-added products. The ANL process could use commercially available heat-treating equipment with minor modifications, and it is ready for testing on a larger scale once enough PMC scrap is available.

Future Direction

- Recommend that the process be demonstrated on a larger scale once large quantities of PMC scrap become available. Large-scale testing, field demonstration of the process, and production of large enough quantities of recovered fibers to make a variety of quality products is necessary to determine the application limitations of the recovered fibers and their fair market value.

Testing of the Process Using PMC Panels Made with Well-Characterized Fibers

Hexcel corporation supplied PMC panels with known properties for carbon fiber recovery tests. We processed some of these panels under different operating conditions and sent the recovered fibers back to Hexcel for evaluation and comparison of their properties before and after recovery. Hexcel¹ found that “The surprising results were the high shear strength of the recycled materials. These shear strength results indicated that the recycling process had small effects on the surface treatment conditions of the fibers. This reveals that the recycled fibers may not

require to be surface treated again. The recycling process may activate the fiber surfaces.”¹ Based on the results of these tests, appropriate recovery conditions that resulted in minimal changes in fiber properties were established. These conditions were then used to recover fibers from similar panels (Figure 1). Hexcel then used the recovered fibers as-is to fabricate new panels of equivalent geometry as the virgin panels and compared their properties with those of the panels from which the fibers were recovered. The data showed a reduction of only 10% in panel stiffness and ~12% in short beam strength. The panels also showed about 50%



Figure 1. Carbon fibers recovered from PMC scrap.

reduction in strength and elongation. Obviously, during the treatment process and handling of the recovered fibers afterward in the hood, some of the fibers were lost; and some lost their original direction and place.

Therefore, the recovered fibers could be used in many applications that require chopped fibers, such as sheet molding compounds or preform products like those made in the slurry process to manufacture automobile parts.

ORNL⁶ also conducted extensive analysis of the recovered fibers and found that the recovered fibers had characteristics similar to those of the original virgin fibers. For example, the density and diameter of the recovered fibers were essentially the same as those of the virgin fibers, and the morphology of the recovered fibers was nearly identical to that of the virgin fibers.

These data prove that at the appropriate processing conditions, the thermal treatment process does not degrade the morphology in the interior constituent material. The recovered fibers also exhibited high shear strength and high oxygen concentration on the fiber surface,^{1,2,6} indicating that the recovered fiber should adhere well to matrix resins without the need for additional surface treatment. The surface chemistry of the recovered fibers was similar to that of the treated virgin fibers (Figure 2). Surprisingly,

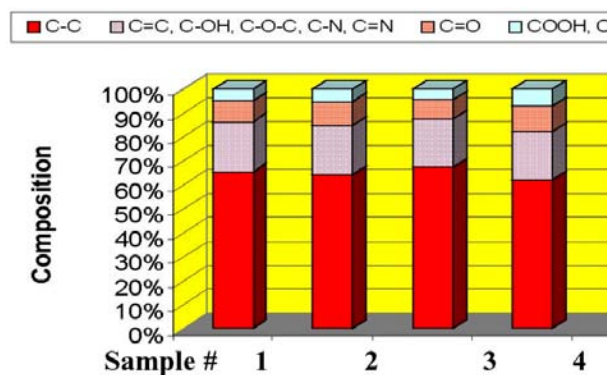


Figure 2. Comparison of functional groups chemistry on the surfaces of ANL recovered fibers (1,2) and virgin untreated (3) and virgin treated (4) fibers (Ref. 2).

some of the recovered fibers exhibited higher concentrations of elemental oxygen at and just beneath the fiber surface than the corresponding virgin control fibers. ORNL concluded that “the recovered carbon fibers from the ANL-pyrolytic based process—exhibit higher O/C chemical ratios than the corresponding virgin, treated but unsized—(finished product) carbon fibers. At the first moment, this result could indicate that these recovered fibers very likely will not require additional surface retreatment.”² Avoiding the need for retreatment of the fibers saves about \$0.40/lb of fibers. “The most significant observation is that the ANL-recovering process yields fibers where all the four peaks are present.”²

During FY 2003 we treated additional panels as well as other PMC scrap made with different carbon fibers and different substrates, including nylons, to identify conditions that would result in degradation of the fibers as evidenced by their oxidation. The results indicated that at temperatures above 1200°F in the presence of “enough” air, oxidation of the fibers did occur after the substrate was essentially removed. The degree of oxidation increased as the amount of air (oxygen) in the thermal reactor was increased. This was the case with all PMC samples tested. Therefore, the process design should take in consideration the need for oxygen in the reactor to oxidize the substrate

and its decomposition products, but the air supply rate should be kept at a minimum during the treatment of the residual substrate after the bulk of it is removed in order to prevent the oxidation of the fibers. In addition, when a mixture of different PMC scrap was treated, the energy released by the decomposing and oxidizing substrate was more than enough to drive the process. As a matter of fact, the temperature in the reactor was exceeding the set point by as much as 100°F. Therefore, the process design should take in consideration the need to manage the changing amounts of thermal energy released during the process as different PMC scrap materials are treated.

Recovery of Carbon Fibers for Reuse in an Automotive Application

During the previous reporting period, arrangements were made with Hexcel to provide ORNL with carbon fibers having known properties to make PMC samples for us to recover their carbon fibers for reuse in making “skid plates” for SUV application. During this reporting period, ORNL made the PMC scrap panels, and we processed about 80 lb of these panels and recovered carbon fibers from them. More than 20 lb of recovered fibers were sent to ORNL to use in manufacturing skid plates for SUVs using the Budd slurry process.

Disposal and Treatment of the Effluent Gas Stream

Work done on this topic during prior reporting periods showed that, as expected, different substrates generate different pyrolysis and oxidation products, including volatile and semivolatile organic compounds. Previously, we analyzed the gases and vapors generated during the thermal treatment of PMC scrap. The analysis showed that carbon monoxide and volatile and semivolatile compounds were present. The number, type, and amount of these species depends on the treatment temperature, oxygen availability, and composition of the PMC feed material.

Therefore, an after-burner is required to destroy these species. In FY 2003 we examined an opportunity to recover some of the organic products by condensation followed by distillation, or by other means, especially when they are not required to provide the energy to drive the process. This option is technically feasible. However, its cost-effectiveness depends on the composition of the generated gas, and this depends on the composition of the scrap stream. For example, epoxy resins can generate substantial amounts of acetone that is widely used as a solvent and as a raw material in the synthesis of other chemicals. Acetone can be condensed and/or scrubbed from the gaseous stream using water because it is highly soluble in water.

Updating of the Conceptual Design and Economic Analysis

The thermal treatment process conceptual design developed during previous periods was also updated especially as to controlling the air supply to the reactor. We also reevaluated the economic analysis for a full-scale plant processing 1,000,000 lb/year of PMC scrap (500 lb/h or 10 tons/week). The estimated payback of about 2 years is still valid based on a value for the recovered fibers of \$1.5/lb. This value is used in the analysis assuming that a value of \$3–\$5/lb of virgin fibers is required before carbon fibers are widely used in the automotive industry.

Conclusions

Work conducted on this project demonstrated that the recovery of carbon fibers from PMC scrap is technically feasible and potentially economical. The recovered fibers have properties that make them usable in chopped-fiber applications for making value-added products such as various automobile parts. The process that was developed in this project is now ready for testing at a larger scale. Therefore, the objective of the project was accomplished.

References

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B. Recycling Assessments and Planning

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Objectives

- Establish priorities for cost-effective recycling of advanced automotive technology materials and components.
- Focus long-term efforts on enhanced recovery/sorting procedures and advanced recycling technologies that are the enabling factors in a vision for 100% recyclability.

Approach

- Consult with automotive manufacturers and recycling industries, the U.S. Council on Automotive Research (USCAR) and its affiliates, national laboratories, universities, and other relevant organizations to assess critical recycling needs/barriers.
- Develop a recycling R&D program plan that will serve as a “working document” to guide DOE/FCVT in establishing priority goals, with an initial emphasis on lightweight body and chassis materials.
- Assist DOE in establishing advanced recycling R&D initiatives and provide technical oversight to ensure that priority objectives/goals are accomplished.

Accomplishments

- Prepared a draft 5-year program plan based on the recommendations and priorities identified in the Roadmap and based on an initial planning meeting with the management council of the Vehicle Recycling Partnership (VRP) of USCAR.
- Negotiated a cooperative research and development agreement (CRADA) with the VRP, the American Plastics Council (APC), and Argonne National Laboratory (ANL), as partners, and initiated effort under the CRADA in August 2003.
- Initiated construction on a large-scale pilot separation facility at ANL. This facility will serve as a focal point for the recycle research to be conducted as part of the CRADA with the VRP and APC.
- Developed an Excel-based process cost model that incorporates two primary modules for recovery automotive plastics: the first module includes the unit operations required for

recovering a plastics concentrate from shredder residues, and the second module includes the unit operations required to recover selected plastics from the mixed-plastics concentrates. The second module allows the user to specify the type of plastics that are to be recovered and the number of recovery stages required.

- Initiated an assessment of a new plastics separation technology under development by Salyp NV of Belgium with support from the VRP, APC, and Association of Plastics Manufacturer's of Europe. Controlled tests of this new "thermoplastics sorting" technology are being done using shredder residues from two European and one U.S. location as feed material.

Future Direction

- Continue development of the Recycling R&D Plan through collaboration with the USCAR VRP and associated USCAR affiliates, the APC, the Automotive Parts Rebuilders Association, remanufacturing industries, materials trade organizations, and other appropriate industries involved in automotive recycling.
- Continue ongoing efforts toward the milestones and objectives of the CRADA statement-of-work.
- Continue evaluations of recycling technology progress in Europe and Japan, along with assessments of critical recycling technologies as new needs are identified.
- Continue ongoing project efforts to assist DOE in preparation of planning documents, priority recycling R&D needs, proposal reviews, and related tasks.

Summary

The objective is to establish priorities and develop cost-effective recycling technologies and strategies in support of the DOE FCVT long-term objectives and goals. Automobile recycling is the final productive use of end-of-life vehicles (ELVs). The obsolete car has been a valuable source of recycled raw materials and useable parts for repair because cars have been mass-produced. Today, cars that reach the end of their useful service life in the United States are profitably processed for materials and parts recovery by an existing recycling infrastructure. That infrastructure includes automotive dismantlers who recover useable parts for repair and reuse; automotive remanufacturers who remanufacture a full range of components, including starters, alternators, and engines to replace defective parts; and ultimately, the scrap processor who recovers raw materials such as iron, steel, aluminum, and copper from the remaining auto "hulk" after components have been recovered for recycling. Each of

these activities contributes to the recycling of obsolete vehicles.

Today, less than 25 wt % of obsolete cars is not profitably recoverable for recycling and is therefore landfilled. For the past 10 years, the original equipment manufacturers—Ford, General Motors (GM), and DaimlerChrysler—through the VRP and other organizations including the Aluminum Association, APC, the Institute of Scrap Recycling Industries, Automotive Recyclers Association, Automotive Parts Rebuilders Association, and the federal government have been working both collaboratively and independently to address technical, institutional, and economic issues that currently limit the recycling of ELVs. Progress has been made in understanding some of these issues, and technology has been developed that can impact the level of ELV recycling.

The recyclability of ELVs is presently limited by the lack of commercially proven technical capabilities to cost-effectively separate, identify, and sort materials and components and by the lack of profitable postuse

markets. While nearly 75 wt % of ELVs is currently recycled in some form, the remaining 25% is sent to landfills each year. During the next 20 years, both the number and complexity of ELVs are expected to increase, posing significant challenges to the existing recycling infrastructure. The automobile of the future will use significantly greater amounts of lightweight materials (e.g., ultra-light steels, aluminum, plastics, and composites) and more sophisticated/complex components.

New technology is and will continue to be needed to improve vehicle recyclability. Using the Roadmap as a framework, we will work with the key stakeholders over the next year to structure a suite of projects to be undertaken in this program area.

The Recycling Strategy

The following strategy outline was developed as part of the Roadmap to maximize the value recovered from ELVs.

- Come together as a unified recycling community to cost-share the development of required new technology.
- Incorporate reuse, remanufacturing, and recycling into the design phase for cars whenever possible.
- Recycle as early in the recycling stream as possible, while relying on the market to optimize the value and amount recycled at each step.
- Maintain a flexible recycling process that can adapt to diverse model lines fabricated with different techniques and materials from various suppliers.
- Develop automated ways to recover bulk materials.
- Emphasize R&D on postshred material identification, sorting, and product recovery.
- Focus R&D efforts on materials not recycled today by sorters (e.g., postshred glass, rubber, fluids, textiles, plastics).
- Develop uses for recovered materials (whether in the same or different applications) and testing specifications.

- Encourage investment in the infrastructure needed to achieve the recyclability goal. Build on the existing infrastructure.
- Develop a means to prevent the entry of polychlorinated biphenyls and other hazardous materials into the recycling stream, and promote acceptable limits in shredder residues.
- Consider the recycling requirements of new technologies entering fleets as early as possible.

The 5-Year R&D Plan

Based on the Roadmap and continuing discussions with key stakeholders, a 5-year R&D plan has been prepared. The plan includes the following three focus areas:

Area 1. Baseline Technology Assessment and Infrastructure Analysis

Understanding the state of the art is critical to moving forward. As stated in the Roadmap

... the status of technologies used, existing process capabilities, and the mass balance flow of automobiles at end-of-life is not known with the level of confidence needed to assure that the industry is making the best choices to optimize recyclability. A better understanding of the interrelationships of all steps in the recycling process from a financial perspective will promote development of [the] infrastructure ... analysis of data is needed to better understand the environmental and economic trade-offs.

The focus of the work under this activity will be to develop the tools and document the information necessary to make effective decisions relative to technology needs to facilitate sustainable future vehicle recycling, and to make effective decisions regarding allocation of R&D resources. Research conducted under this area generally addresses the broader priorities of “proactive industry wide-action” and “industry-wide analysis”

for which a number of specific needs are identified in the Roadmap.

In FY 2004, the focus of this area will be on developing a catalogue of available and emerging automotive recycling technologies and preparing an updated assessment of the state of the art of the recycling industry.

Area 2. Materials Recovery Technology Development and Demonstration

Development of technology that can lower the cost of recycling and meet the financial and institutional requirements of the market is critical to improving the recycling rate of automotive materials. Technology development and demonstration is the cornerstone of this program and will serve as the program's focal point. Although research to be conducted in this area will initially focus on addressing technology needs for postshred materials recovery, projects that enhance preshred recovery, including disassembly for materials recovery and direct reuse and remanufacturing of components, will also be included. In the long term, components such as fuel cells, advanced batteries, and hydrogen reformers are more likely to enter the recycle stream through preshred recovery for remanufacturing, repair, and materials recovery. Research will be undertaken to determine the technology needs to ensure the recyclability of these very advanced automotive components. This area of research generally supports the needs of the broad priorities of "lowering the risk of technology development and purchase,"

"preshred recovery," and "postshred material identification and sorting" that are outlined in the Roadmap.

In FY 2004, the focus of this area will be to support development and demonstration of postshred separation technology, building upon the technology development efforts previously undertaken by ANL, the VRP, the APC, and others. Development of technology to cost-effectively sort postshred material is a top-priority need.

Area 3. Recovered Materials Performance and Market Evaluation

Understanding and enhancing recovered materials performance is an essential ingredient to a successful recycling program. This is especially true in automotive systems when the materials and components that are recovered have been in use for an average of 10 to 15 years. This area will include projects to quantify the relative performance of recovered materials vis-à-vis new or virgin materials; research on compatibilization of recovered polymers to improve performance properties; development of technologies to upgrade the recovered materials, such as separation of fibers from polymeric substrates; and development of applications for other recovered materials, such as rubber and glass.

In FY 2004, materials and plastics that are recovered as part of the technology demonstration area of research will be evaluated to define the performance properties of those material vis-à-vis "virgin" materials.